AN X-RAY ABSORPTION SPECTROSCOPIC STUDY OF $YBa_2Cu_{3-x}Fe_xO_{7+y}$

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We report a study of x-ray absorption near-edge structure of the O K and Cu L_3 edges in $YBa_2Cu_{3-x}Fe_xO_{7+y}$ for x = 0.01, 0.05 and 0.15. We attribute the peaks below 529 eV in the O K edge spectra of $YBa_2Cu_{3-x}Fe_xO_{7+y}$ to holes on the O sites. Our results show hole filling with increasing Fe content, which means that Fe enters the structure primarily in the formally trivalent oxidation state. Cu L_3 edge spectra reveal increased amount of Cu^{3+} with increasing Fe content. The results are discussed in terms of charge balancing.

KEY WORDS: High-T_c Superconductors, XANES, XRD, $YBa_2Cu_{3-x}Fe_xO_{7+y}$

INTRODUCTION:

Metallic substitution studies have enhanced our understanding of the superconducting and normal state properties of high-T_C superconductors. Substitution of metals in $YBa_2Cu_3O_{7-\delta}$ (YBCO) usually depresses T_C and has other negative effects on the superconducting properties. The superconducting properties of YBCO depend not only on the oxygen stoichiometry but also on the oxygen ordering. Substitution of Cu can provide a selective tool to investigate the specific effects because depending on the dopant characteristics, the substituted compounds may exhibit modified microstructures without any substantial change in the overall oxygen content. Much work has been done in this direction. Trivalent metal ions like Fe, Co, or Al replace Cu in Cu(1) site on the Cu-O chain and depress Tc more slowly than divalent Zn and Ni which replace Cu in Cu(2) site in the CuO2 plane [1]. Substitution of Cu by Fe may lead to (i) reduction of T_C, (ii) structural transformation with increasing impurity concentration, (iii) increase in oxygen content accompanied by a rearrangement of oxygen, and (iv) local magnetic ordering. When Cu is replaced by Fe, the oxygen atoms might rearrange themselves in order to provide the most stable Fe site. This modifies the local electronic densities of states. Little is known about the variation of electronic structure due to the substitution. Yang et al. [2] have studied the variation of electronic structure of YBCO upon Fe doping, at the Fe site using x-ray absorption spectroscopy (XAS). In this paper we compliment their work by investigating Cu and O sites using XAS. Furthermore, Zhang et al. [3] have studied the same system using x-ray photoelectron spectroscopy (XPS) and found that effective copper valence of the system increases with increasing Fe content. This is in contradiction with the oxygen iodometry results of Awana et al. [4]. We address this issue also in this paper.

While XPS probes the occupied electronic states, XAS probes the unoccupied electronic states in the most direct way. Thus these two experimental techniques compliment each other. With the advent of synchrotron radiation sources, XAS has

become a powerful technique used to investigate the empty states. It allows one to selectively study a particular species in a compound [5].

EXPERIMENTAL:

Stoichiometric amounts of high purity CuO, Y_2O_3, $Ba(NO_3)_2$ and Fe_2O_3 (at least 99.9%) were mixed followed by grinding in an agate mortar. The mixer was preheated at 1173 K for 18 hours. After regrinding the black powder, it was pressed into pellets of 1 cm diameter and heated at about 1203 K twice for 35 hours with intermediate grinding. The final annealing of the samples was performed at 1223 K for 24 hours in oxygen atmosphere, followed by slow cooling of the samples to 823 K and keeping it for 50 hours. Finally the samples were furnace cooled to room temperature in oxygen atmosphere. In this way, poly crystals of $YBa_2Cu_{3-x}Fe_xO_{7+y}$ with starting x values of 0.01, 0.05 and 0.15 were prepared.

The critical temperatures of these samples were determined by standard four-probe technique, using a constant current source and a Keithly-181 nano voltmeter. X-ray diffraction patterns of the samples were obtained using a Phillips PW1700 automated diffractometer. The analysis is computer assisted so that the interplanar spacing values can be corrected for the instrument error function by analyzing a silicon standard and subsequent phase identification.

X-ray absorption near edge structure (XANES) measurements were performed using Advanced Light Source at Lawrence Berkeley National Laboratory on beamline 9.3.2 [6]. High-resolution XANES spectra were taken in the Ba M, Cu L_3, Fe $L_{2,3}$, and O K absorption edge regions, while the monochromator was set at a resolving power (E/ΔE) of $\geq$ 7000. The photon flux at the sample was about 10^{10} photons/s. The YBa_2Cu_3-

$_x Fe_x O_{7+y}$ poly crystal samples were cooled to about 90 K before scraping them in a vacuum of about 1×10^{-10} torr, in order to minimize oxygen loss from the fresh surface [7]. Note that cooling the sample below its T_c is not necessary for the scope of this study. Since the size of the synchrotron radiation photon beam at the sample was ≤ 1 mm, it was not difficult to align the system to make sure that only the sample was illuminated by the photon beam. XANES measurements were performed using a partial electron yield detector consisting of 40 mm channel plates in the pulse counting mode. I_0 signal from a freshly evaporated gold grid was used for normalization of spectra.

RESULTS AND DISCUSSION:

The samples used in this investigation were first characterized by monitoring their resistance as a function of temperature using the standard four-point contact method. The zero-resistance transition temperatures were 93, 92 and 71 K for x = 0.01, 0.05 and 0.15 respectively. The XRD patterns for all the samples are shown in Fig.1. Further XRD indexing and refinement was performed using a Powder Diffraction Package (PDP) program [8] which confirmed that they are all single phase with orthorhombic symmetry. This is clear from the (012) and (102) peaks. Although these two peaks get closer to each other in the sample with x = 0.15 they are still distinct. This means that the sample with x = 0.15 is still orthorhombic. This is consistent with the resistivity measurements that revealed all three samples were superconducting.

Fig.2 shows the O K edge of $YBa_2Cu_{3-x}Fe_xO_{7+y}$ (YBCFO) poly crystals at 90 K as a function of x. Energy scale was corrected by comparing Ba M edge of the samples with that of $YBa_2Cu_3O_{7-\delta}$ single crystal [9], with the assumption that the Fe substitution does not affect Ba site. A straight line fitted to the region before the peaks (below 523 eV) has been subtracted as background. The spectra shown in the figure have not been smoothed or filtered in any way. Two small peaks at 524.5 and 526.5 eV (labeled A and

B respectively) and a prominent peak at 530 eV (labeled C) precede the main edge which starts at about 531 eV. Multiple scattering calculations assign peak A and B to holes in O sites in the CuO2 plane (O2 and O3) and Cu-O chain (O1) respectively [9]. Intensity of peaks A and B decreases with increasing Fe content, indicating hole filling in both CuO2 plane and Cu-O chain. This result is in good agreement with M. Karppinen et al. and I. S. Lyubutin et al. [10,11]. This seems to support that T_c degradation with increasing iron substitution is due to hole filling. In other words, Fe enters the structure primarily in the formally trivalent oxidation state. We interpret the peak C as the signature of the O holes being removed and localized around the Fe sites in the compound. Note that the intensity of this peak increases with increasing Fe content. Our interpretation is further supported by the general observation that many of the insulating transition metal oxides exhibit such sharp peaks between 529 and 530 eV in the O K edge spectra [12]. Furthermore, the peak C resembles CuO rather than Iron oxide, suggesting that Fe actually enters Cu site.

Fig.3 shows the Cu L_3 edge of $YBa_2Cu_{3-x}Fe_xO_{7+y}$ poly crystals at 90 K as a function of x. The spectra were acquired with 2-bunch beam implying less than 10^{10} photons/s at the sample. Again the energy scale was corrected using Ba M edge as stated earlier. The spectra clearly show a small peak at about 931 eV along with the main peak at about 929.5 eV. Note that the peaks shift to higher energy with increasing Fe content. This indicates that the average valency of Cu increases with increasing Fe content. While the main peak is ascribed to a transition from the $3d^9$ ground state (formally Cu^{2+}) the higher energy shoulder is a signature of Cu^{3+} in the CuO2 layers [13-17]. Cu can be found in the formal valence states of +1 (e.g. CuO_2), +2 (e.g. CuO), and +3 (e.g. $NaCuO_2$). Note that the integer valences are only meant to describe a nominal configuration of Cu, with covalency effects not included. The ground state of Cu^{1+} is a $3d^{10}$ configuration, whereas that of Cu^{2+} is a mixture of $3d^9$ (~60%) and $3d^{10}\underline{L}$ (~40%) configurations [18], where $\underline{L}$ denotes an oxygen ligand hole, and that of Cu^{3+} is a mixture of $3d^8$ and $3d^9\underline{L}$ configurations [19]. It is, however, known from x-ray

photoemission spectroscopy (XPS) data that in CuO, which is electronically not too different from the situation found in the CuO2 layers in the cuprates, the $3d^8$ configuration is about 10 eV above the $3d^9+3d^{10}\underline{L}$ ground state [20]. Therefore, if formally Cu^{3+} ions are present, their wave functions will be dominated by the $3d^9\underline{L}$ component because of the high excitation energy of the $3d^8$ component. The components $3d^9$ for Cu^{2+} and $3d^9\underline{L}$ for Cu^{3+} are almost degenerate [20]. This can rationalize the difficulty in detecting Cu^{3+} in the Cu 2p XPS spectra. Nonetheless, we have clearly observed the signature of Cu^{3+} in our x-ray absorption measurements at the Cu L_3 edge. Intensity of this Cu^{3+} peak increases with increasing Fe content. This confirms the XPS results by Zhang et al. [3]. In pure YBCO increased Cu^{3+} is taken as a sign of increased hole concentration and thus improved superconductivity. However, in YBCFO T_c decreases with increasing x because of increased O content. Therefore, in YBCFO increased Cu^{3+} is only due to charge balancing.

CONCLUSIONS:

In summary, our high-resolution XANES spectra at O K edge in $YBa_2Cu_{3-x}Fe_xO_{7+y}$ for x = 0.01, 0.05 and 0.15 show hole filling with increasing Fe content in both CuO2 plane and Cu-O chain. Our Cu L_3 edge spectra reveal increased amount of Cu^{3+} with increasing Fe content, which is due to charge balancing.

ACKNOWLEDGMENTS:

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FIGURE CAPTIONS:

FIGURE 1:   XRD patterns of $YBa_2Cu_{3-x}Fe_xO_{7+y}$ poly crystals for x = 0.01, 0.05 and 0.15.

FIGURE 2:   O K edge of $YBa_2Cu_{3-x}Fe_xO_{7+y}$ poly crystals at 90 K as a function of x.

FIGURE 3:   Cu L_3 edge of $YBa_2Cu_{3-x}Fe_xO_{7+y}$ poly crystals at 90 K as a function of x.